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(54) Electroplating non-metallic surfaces

(57) In a method for electroplating non-metallic surfaces on a substrate (e.g., of plating hole walls in metal clad laminates), metallic sites are formed on the surface to be plated and the resulting site-containing surface is electroplated by means of an electroplating bath comprising a component (e.g. a dye, surfactant, chelating agent, brightener, levelling

agent or pyrophosphate ions) which causes the plating to preferentially occur at the sites in comparison to the plating on surfaces of the same metal as the one plated out; whereby an increased rate of plating on the site surfaces is achieved with respect to the plating reaction on a surface consisting of the metal to be plated out.

The method allows non-metallic surfaces to be rapidly and uniformly electroplated, without the need to electrolessly plate the surfaces first.

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FIG.1

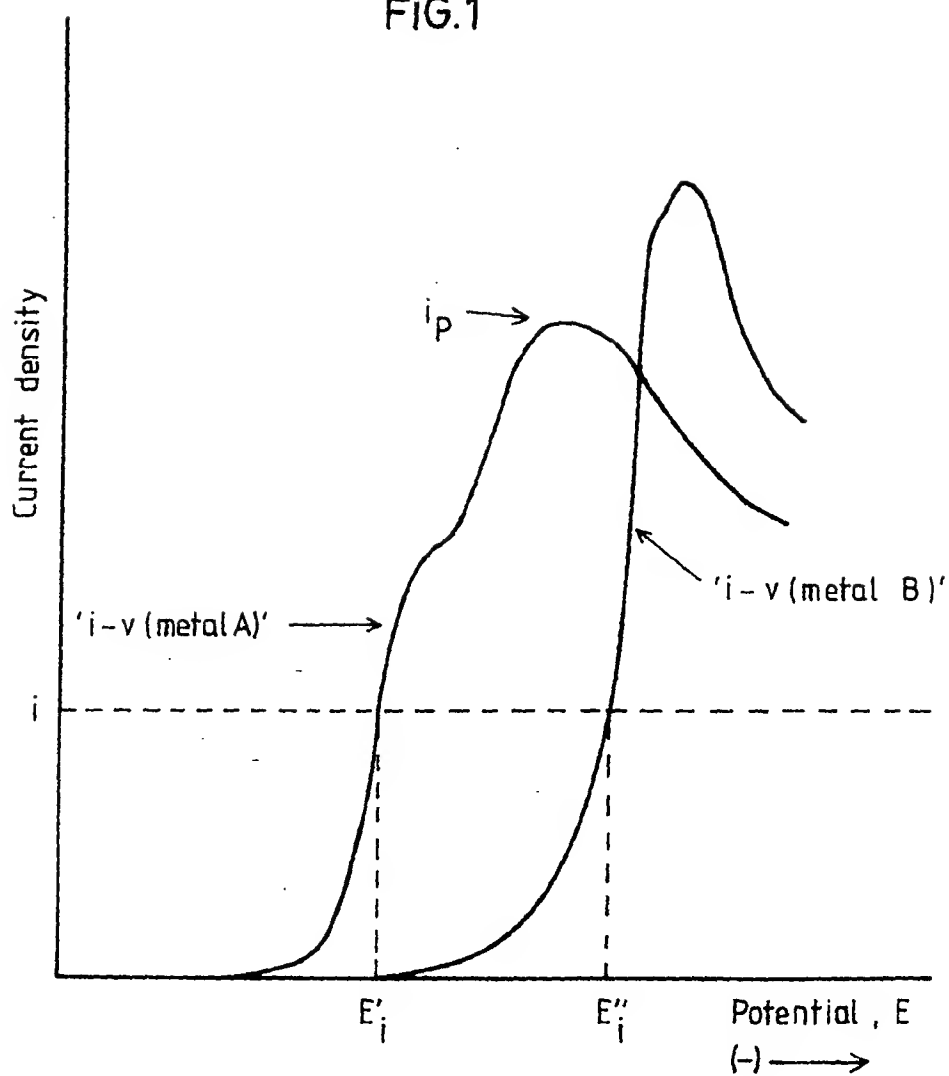
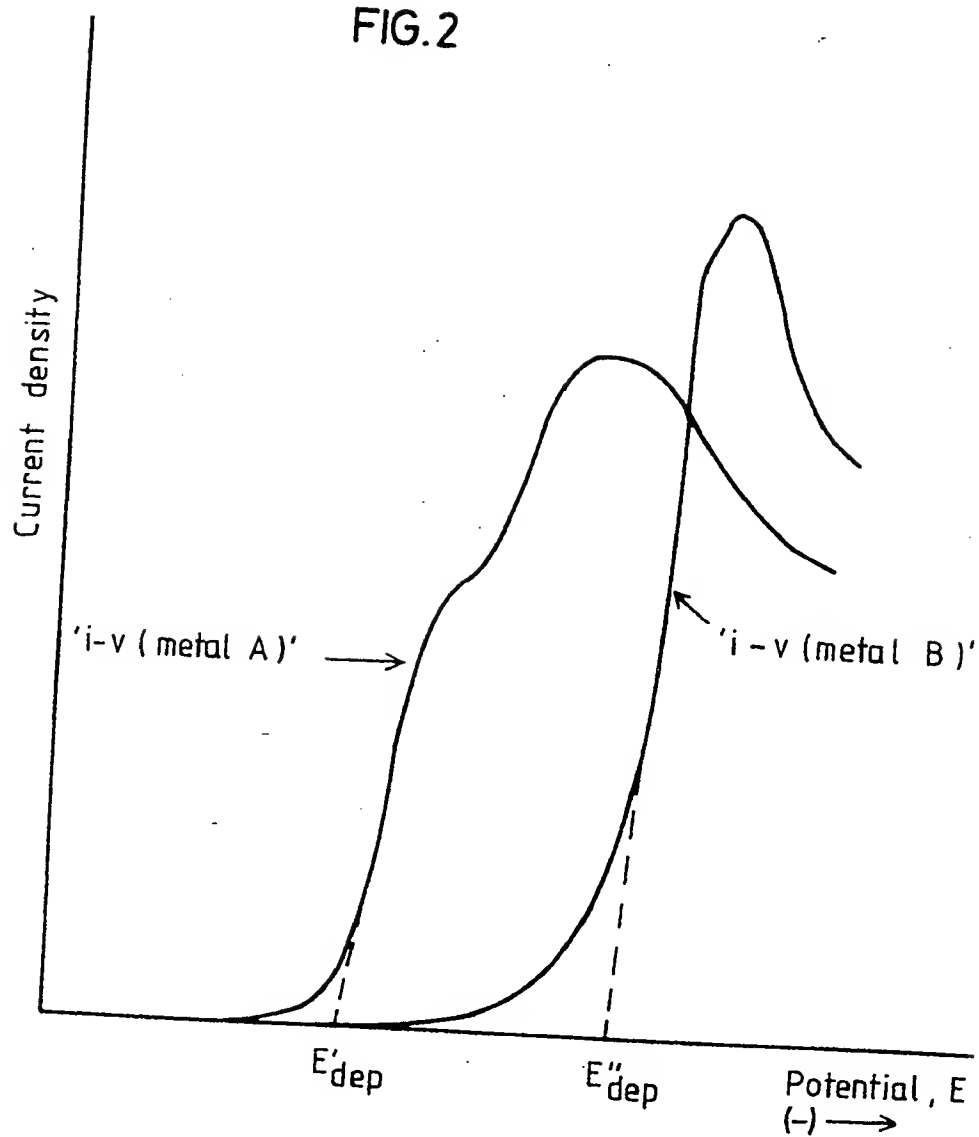


FIG. 2



3/4



1 MINUTE
FIG. 3a

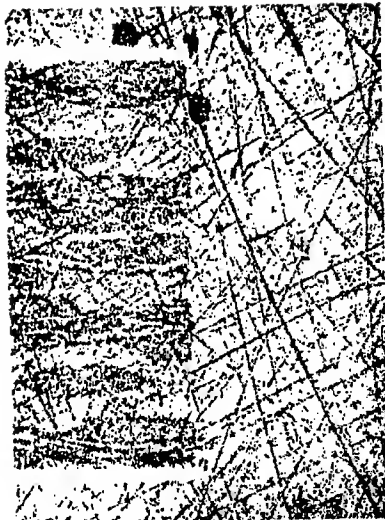


2 MINUTES
FIG. 3b



3 MINUTES
FIG. 3c

4/4



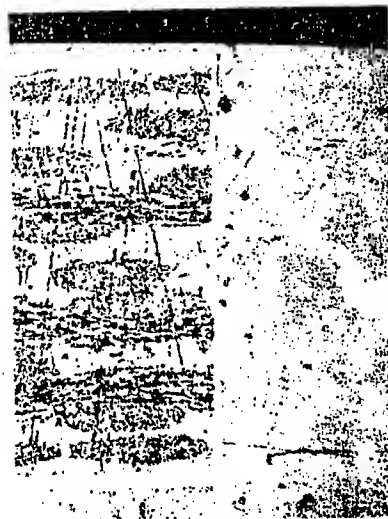
4 MINUTES

FIG.3d



5 MINUTES

FIG.3e



20 MINUTES

FIG. 3f

SPECIFICATION

Impr ved method for electroplating non-metallic surfaces

The present invention relates to metallizing non-conductors. It also relates to the manufacture of printed wiring boards with holes having metallized walls, hereinafter referred to as plated-through hole printed circuit boards. In particular, it concerns methods of electroplating insulating surfaces and the composition of the electroplating solutions used for this purpose.

Non-metallic surfaces are usually metallized by first making the respective surface catalytically receptive to electrolessly formed metal deposits and subsequently exposing the thus catalyzed surface to a plating bath solution of the kind operating without an external source of electricity and for a time sufficient for forming a metal-, e.g., Cu- or Ni-layer of desired thickness. This initial layer is usually provided with additional metal deposits formed by conventional electroplating. In well known methods for making plated-through hole printed circuit boards, this metallizing concept and its variations are employed for metallizing hole walls. In the version starting with two-sided copper clad laminate as the base material, a panel of suitable size is first provided with the required holes, and the hole walls are rendered catalytically receptive by immersion in a known catalyst solution. Subsequently, a metal-, usually copper-deposit is formed by exposure to a bath solution which produces metal deposits without an external source of electricity, generally known as electroless plating baths, and for a time sufficient to achieve a thickness of, e.g., 0,5 to 2,5 μm . This initial, conductive metal-layer is further plated up by means of conventional electroplating.

The typical catalyst solutions employed in the aforescribed methods have been used in this industry for many years and have been developed to a relatively high degree of stability. Surfaces treated with such solutions catalytically promote the generation of electrolessly formed metal deposits by the oxidation of suitable components present in the electroless plating bath with this mechanism acting as an internal source of electrons to be used in the plating reaction for reducing complexed metal ions to metal.

Operation of electroless metal plating solutions requires rather careful monitoring of the different components and replenishing of used up materials by controlled addition of chemicals. Furthermore, the said plating solutions have a tendency to indiscriminate deposition thus forming metal-, e.g., copper-deposits on walls and the bottom of tanks used for operating such plating baths. This necessitates frequent interruption of the plating operation, removal of the plating solution from the tank and cleaning the tank walls and bottom by means of an etching operation.

Electroless metal plating is, therefore, rather expensive and complex and needs highly trained operators.

In spite of these substantial shortcomings, electroless deposition of an initial layer of metal has, up to now, been an integral part of all processes used for metallizing non-metallic surfaces including such processes employed in the manufacture of printed circuit boards.

In US Patent 3,099,608 is described the use of a palladium-tin-chloride colloid to form an essentially non-conductive film of colloidal or semi-colloidal particles on the hole walls made in a laminate used to make printed circuit boards; and of electroplating for copperizing said hole walls. The process according to US patent 3,099,608 has, however, severe shortcomings and was found to be not applicable for practical use. The palladium-tin-chloride colloidal suspension has an unacceptably short life span. It can only be used for about nine days due to coagulation of the suspension, and because of its high palladium content it is rather expensive. Furthermore, the method according to 3,099,608 deposits substantially more copper on the surface than on the walls of through-holes and is, therefore, unacceptable for commercial use.

US patent 3,099,608 is based on the use of a "thin, barely visible film of particles" of "semi-colloidal palladium" deposited on the surface to be plated, said film having "substantial resistance", and on the teaching, "that the palladium being by nature both a catalytic metal and a conductive metal, has potentialities for simultaneous and combined activating and conductive functions" (column 4, lines 53 to 56) and, further, that "After the electroplating is started at a conductor it is activated apparently by the catalytic properties of the palladium and the electrodeposition process proceeds directly on the film of conductor particles" (column 4, lines 62 to 66). At column 5, lines 2 to 7, it is stated that "Since the colloidal palladium deposit in the through holes was an extremely poor conductor to serve as a base for the electroplating as compared with the deposited graphite, something else must have aided in the electrodeposition, i.e., a catalyst must have aided in the plating reaction". In spite of the fact that the inventors' observation dates from 1959 and, consequently, is contemporary with the use of graphite for metallizing non-conductors and with the first application of the "seeder-electroless plating technology" for metallizing plastic parts and making plated-through-hole (PTH) boards, it did not result in a process of any practical use. Considering the substantial initial difficulties with the seeder-electroless plating technology and its development, and, further, the continuing complexity characteristics of electroless plating bath operation, control and maintenance, when compared to the comparatively simple electroplating process, it is rather most surprising that the observations of the inventors of 3,099,608 were of no impact as far as the technological development of the last two decades is concerned. The reason is, that these observations did not result in a teaching which allows

the average person skilled in the art to make use of it. Lacking this teaching, the inventor's observations could only be duplicated when using their "conductivator solution" and the copper pyrophosphate electroplating bath existing at the time.

It is believed that the inventors of 3,099,608 did not recognize the importance of the composition of the copper electroplating bath. For example, of the known formulations for pyrophosphate electroplating baths employed at the time of filing the US patent, the simplest one did not produce copper of adequate quality for printed circuit boards; the more complex type of bath did produce adequate copper quality, but inhibits the working of the process suggested in 3,099,608. The industry, therefore, found the observations made by the inventors and described in US 3,099,608 to be of no practical use. The "seeding-electroless copper plating" followed or not by electroplating was, consequently, accepted as the only approach for metallizing non-metallic surfaces available to the art.

US 3,099,608, therefore, teaches away from the present invention claimed by applicant. To arrive at this invention, the misconception presented by the inventors of 3,099,608 that the characteristics of the electroplating baths were not critical, had to be overcome and completely discarded.

In accordance with the present invention there is disclosed a method for metallizing non-metallic surfaces by electroplating in a vessel provided with a counter-electrode and containing an electroplating bath solution comprising in ionic form a metal (B) to be electroplated, said surfaces being provided with a connector area, said connector area being located outside of the non-metallic surface area to be electroplated, characterized by the steps comprising (a) forming a plurality of metallic sites on said surfaces, said sites comprising or consisting of a metal (A), said metal (A) being different from said metal (B) to be deposited on said surfaces by electroplating; and (b) exposing said surfaces including at least a portion of said connector area to the electroplating bath solution, said solution having a defined conductivity and further comprising one or more component(s) (C) which cause preferential deposition of metal (B) on said metallic sites comprising or consisting of metal (A), compared to the deposition on surfaces consisting of, or formed by, the species of the electrodeposited metal (B); and (c) applying a potential to the connector area and the counter electrode which is sufficient to initiate and cause preferential deposition metal (B) on said sites comprising or consisting of metal (A), for a time sufficient for forming a substantially uniform deposit of desired thickness.

In one embodiment, the rate of deposition on the metallic sites is at least one order of magnitude greater and preferably two orders greater than the rate of deposition on the plated-out metal.

In another embodiment, the metallic sites (A) and the metal (B) to be electrodeposited are comprised of metals selected from Groups Ib or VIII of the Periodic Table of Elements provided that they are not the same.

In still another embodiment, the component (C) referred to above is selected from dyes, surfactants, chelating agents, brighteners or levelling agents.

In yet another embodiment, the substrate provided with metallic sites is exposed to one or more of the following treatments: heat treatment, treatment with a cleaner conditioner, and/or treatment with a reducing agent.

The method disclosed and claimed in the present invention is an improved method of plating non-metallic surfaces on a substrate. More particularly, it is a highly effective method for plating through-hole walls in metal clad laminates.

A special advantage obtained in the manufacture of plated-through-hole printed circuit boards in accordance with the present invention is the integrity of the copper hole wall. Since the copper is electroplated directly on the non-metallic hole wall substrate without an intervening electrolessly formed metal layer, the physical properties and adhesion at the copper-plastic interface as well as the adhesion between foil copper and the electroplated metal-, e.g., copper-deposit, are greatly improved. This is particularly important in the manufacture of high reliability printed circuits such as multilayers.

In practice, the method of this invention for electroplating non-metallic surfaces on a substrate involves the steps of forming discrete metallic sites on the surface to be plated in which said metallic sites are of a metal species different from the species of the metal to be electroplated, providing a connector area on said substrate and outside the non-metallic surface area to be electroplated, contacting said surface to be plated and at least part of the connector area with an electroplating bath solution which contains a plateable metal of the species to be electrodeposited and a component which allows preferential deposition of said metal to be deposited on said metallic sites over plated-out metal from said electrodepositing metal, providing a vessel containing the electroplating bath solution with a counter-electrode, and applying a potential between the electrodes formed by said connector area and said counter-electrode sufficient to initiate and cause preferential deposition on the surface provided with said sites for a time sufficient to form a deposit of desired, substantially uniform thickness.

Without intending to be bound by any particular theory, it is applicant's belief that the direct electroplating process claimed herein is based on the following principles:

1. (1) Metallic sites provided on non-metallic surfaces are connected to a "connector area" (connector electrode) also provided on said surface by the plating bath electrolyte forming a "resistive path" between the connector area and the neighboring sites; similar paths are

formed between the sites. The higher the density of the metallic sites, the faster the uniform metal layer is formed by electrodeposition.

- (2) The higher the conductivity of the electrolyte the lower the resistance of the "resistive path"; with a theoretical electrolyte of infinite conductivity, all sites would be at the same potential as that of the connector area. Conversely, with a theoretical electrolyte of very low conductivity, the resistance between sites and the connector area would for all practical purposes be too high for developing a potential for plating on the sites.
- (3) With practical electrolytes, a voltage drop develops on the resistive path. Thus, based on the foregoing,
 - (a) the potential supplied by the power source to the counter-electrode and the connection area has to be selected so as to compensate not only for the voltage drop between the electrodes including the deposition overvoltage, but also for the voltage drop on the resistive path formed by the electrolyte so that the adequate plating potential is supplied to the metallic sites;
 - (b) the higher the electrolyte conductivity, the faster is the plating reaction on the sites (and also the more uniform in thickness);
 - (c) the conductivity of the electrolyte should be selected as high as acceptable with respect to plating parameters.
- (4) Component (C) present in the electroplating bath causes the forming of an initial electrodeposit preferentially growing laterally along the surface provided with said metallic sites compared to the vertical growth on the surface of the plated out metal.

The term "conductivity" as used herein is defined as a function of the concentration of the current carrying species, i.e., in an acidic bath, the hydrogen ions are assumed to act as the main current carrying species.

- II. (1) For all practical purposes, it is imperative that the deposit formed by electroplating is substantially uniform and that its thickness is substantially not a function of the distance to the connector area. In the case of printed circuit boards with holes having metallized walls, the deposit on the surface and the one on the hole walls should not be of substantial, inadmissible difference in thickness.
- (2) The problem of non-uniformity also exists for electroplating in general. To overcome it, certain additives are used in the plating bath solution known, e.g., as leveling agents.
- (3) Pyrophosphate electroplating baths comprising such additives produce satisfactory results if used in the standard "seeding, electroless-electroplating" process.
- (4) Copper pyrophosphate baths of the additive comprising type, available at the time, rendered the process suggested in US 3,099,608 inoperative. The reason for this is that the additives commonly used attach themselves equally on the metal of the species plated out (copper) and the palladium of the metallic sites or, even preferentially, attach themselves to the latter thus interfering with or inhibiting the plating operation on said sites. Rather unexpectedly, in the light of US 3,099,608, applicant obtained satisfactory results as far as both uniform thickness and superior quality of the metal deposit are concerned, by employing bath formulations comprising one or more components which preferentially attach themselves to the species of the metal to be plated out thus reducing the plating action on said surfaces if compared to the plating action on the metallic sites of a different, suitable metal, e.g., palladium, or by preferentially attaching themselves to the metal of the metallic sites and increasing the plating action on said sites if compared to the surface of the species of the metal plated out.

The problems described above with respect to the use of the seeding, electroless-electroplating process as well as the inoperative procedure described in US patent 3,099,608 are completely overcome by the invention claimed in the present application.

- As is evident from the above theorized mechanism, the potential applied must be sufficient to electrodeposit said plateable metal on said discrete sites at a rate faster than on the plated out metal. In practice, this potential is determined by well-known and accepted electrochemical techniques.

- One such technique involves measurements of the current potential relationships for the electrodeposition of a metal on various substrates in the absence and presence of the component (C). In the potential range applicable in standard electrodeposition solutions (e.g., for a copper sulfate and sulfuric acid plating solution, approximately 0 to -200 mV vs saturated calomel electrode, and for a copper pyrophosphate plating solution, approximately -300 to -1000 mV vs saturated calomel electrode), it is found that the rate of plating on various substrates provided with metallic sites is faster when the plating solution contains component (C) compared to the rate of plating on other substrates with surfaces of the metal which is to be plated out.

- Adsorptive components (Component (C)) of the electroplating solution can be selected on the basis of the current potential curves obtained with an electrode made of the electroplating metal, e.g., copper, and with the electrode made of the metal employed for forming the metallic sites (e.g., palladium). Current-potential curves are recorded using the three-electrode system comprising the test, the counter, and the reference electrodes. Electrode polarization can be performed by applying a

linearly changing potential and recording the current (voltametric method), or by applying a constant current and recording the potential (galvanostatic method). Description of the three-electrode system, voltametric and galvanostatic methods are given in "Modern Electrochemistry" by J. O. M. Bockris and A. K. N. Reddy, published by Plenum Publ. Corp., New York, NY, 1970, pages 891—893 and 1019—

5 1026. 5

A rapid method for selecting the bath composition for the process of this invention uses current-potential curves to evaluate the difference ΔE_i , which is defined by $\Delta E_i = E'_i - E''_i$, wherein E'_i and E''_i are potentials, at the current density i , of the electrode made of the electroplating metal and the metal employed for forming the metallic sites, respectively (Fig. 1). The current density i is in the 10 range of 30 to 50% of the peak current i_p (Fig. 1). With the current density selected in this way the 10 electrode made of the metal employed for forming the metallic sites is not substantially covered by the plating metal at the E_i potential. The current density i in the galvanostatic method is selected also in a way such that there is non-substantial coverage of the electrode made of the metal employed for forming the metallic sites with the plated metal.

15 The procedure for selection of the adsorptive components consists of the following steps: 15

- (1) Record current-potential ($i-v$) curves for the two types of test electrodes, the electroplating metal (e.g., copper) and the metal employed for forming the metallic sites (e.g., palladium);
- (2) Select current density i in the range of 30 to 50% of the peak current;
- (3) Read potentials E'_i and E''_i for the selected current from the current-potential curves ($i-v$);
- 20 (4) Calculate the difference in potentials $\Delta E_i = E'_i - E''_i$; 20
- (5) Adsorptive components causing a high ΔE_i value are the preferred components, i.e., a bath with a high value of the difference ΔE_i is a preferred bath. The same method and criterion is used to select the preferred concentration of the adsorptive component.

Another rapid method for selecting the bath composition for the process of this invention also 25 uses current-potential curves, but in this case the function ΔE_{dep} is determined, with this function 25 defined by $\Delta E_{dep} = E'_{dep} - E''_{dep}$, where E'_{dep} and E''_{dep} , respectively, are the deposition potentials (i.e., the potentials extrapolated to zero current from the current-potential curves) for the plateable metal on the substrate made of the electroplating metal and for the metal employed for forming the metallic sites (Fig. 2).

30 The experimental method is the same for this techniques as for the previously described method. 30 However, E'_{dep} and E''_{dep} are calculated by extrapolating the current-potential curves to zero current and then reading the values of E'_{dep} and E''_{dep} . In this procedure, a bath composition with a high ΔE_{dep} value is a preferred bath composition. Adsorptive components concentrations causing a high ΔE_{dep} value are the preferred concentrations for these components. All of these quick methods for 35 selecting bath composition for plating at the constant current can be modified for the use in other 35 techniques of metal plating, such as pulse plating, fast galvanostatic or potentiostatic plating. Besides the above described quick methods for selecting bath composition for the process of this invention, other methods (described in "Modern Electrochemistry", pages 1017 and seq.) may be used.

Accordingly, any component which causes the plating rate to be faster on the metallic sites than 40 on the plateable metal as described above is within the scope of this invention. In one embodiment of 40 the present invention the component (C) effects preferential deposition by preferentially attaching itself to a surface of the species of metal (B) if compared to the surface of the species of metal (A) thus substantially inhibiting or reducing the plating reaction on surfaces formed by metal (B) without substantially interfering with the plating reaction on surfaces formed by the species of the site metal 45 (A). 45

In another embodiment, component (C) preferentially attaches itself to the species of the site metal (A) with said attached component (C) reducing the overpotential and thus increasing the plating reaction if compared to said reaction on surfaces of the species of metal (B).

In accordance with a preferred embodiment of the invention, the conductivity of the 50 electroplating bath solution and the potential applied to the connector area and the counter electrode 50 are selected sufficiently high to achieve a rate of deposition on the surface of the species of the site metal (A) which is at least one order, and preferably two orders of magnitude higher than the deposition rate on the surface of the species of metal (B). It was found that the maximum conductivity suitable for the process of this invention is for all practical purposes as high as permissible with 55 respect to the other plating parameters. 55

It was also found that the potential applied to the electrodes has to be selected to compensate for the potential drop on the resistive path formed by the plating bath solution between the connector area and the metallic sites consisting of, or comprising metal (A), and between such neighboring sites.

Moreover, it is preferred that this potential be selected at the highest value permissible with 60 respect to the other plating parameters. 60

Metal (A) as well as metal (B) may be selected from Groups Ib or VIII of the Periodic Table of Elements provided that they are different.

Preferably, metal (A) and (B) are selected in such a way that metal (A) displays a lower plating potential than metal (B) under the conditions provided by the plating operation.

Preferred metals for (A) are selected from palladium, platinum, silver and gold with the most preferred being palladium.

Preferred metals (B) are selected from copper and nickel.

The preferred electroplating bath solutions are acidic.

5 Component (C) may be selected from dyes, surfactants, chelating agents, brighteners and leveling agents which preferentially attach themselves to surfaces comprising or consisting of metal (B) and acting by reducing or inhibiting the plating reaction and/or form depolarizing agents preferentially attaching themselves to surfaces consisting of metal (A) and increasing the plating reaction on said surface. 5

10 Suitable dyes are, e.g., the ones selected from Victoria Pure Blue F80, methylene blue, methyl violet, acid blue 161, alcian blue 8GK, and other N-heterocyclic compounds, triphenylmethane type dyes and aromatic amines, imines, and diazo compounds including fused ring amines, imines, and diazo compounds. Suitable surfactants include nonionic surfactants such as alkylphenoxy polyethoxyethanols, e.g., octylphenoxy polyethoxyethanol, and nonionic fluorocarbon surfactants such as Zonyl FSN^{RTM}. 10 15

Among the many surfactants including wetting agents and water soluble organic compounds proposed for use in electroplating solutions, are surfactants and polymers containing polyoxyethylene. Compounds containing as low as four and as high as one million oxyethylene groups have been found to be effective. A preferred group of said compounds includes polyoxyethylene polymers having as few as twenty and as many as one hundred fifty oxyethylene groups. Also preferred are block copolymers of polyoxyethylene and polyoxypropylene. Among these preferred block copolymers are those containing from seven to two hundred fifty oxyethylene groups. In general, it has been found that these polyoxyethylene compounds when added to an electroplating bath solution, particularly an acidic electroplating bath solution, will greatly enhance the growth of electroplated metal (B) on the non-conductor surfaces provided with said metallic sites (A). Most frequently, these polyoxyethylene compounds are used in the electroplating bath solutions in a concentration range of 0,1 to 1,0 g/l. The optimum concentration depends on the composition of the electroplating bath solution and the polyoxyethylene compound selected. In some cases less than 0,1 g/l or more than 1,0 g/l may be preferred. 20 25

30 Representative chelating agents include riboflavin, 2,4,6-(2-pyridyl)-s-triazine and the pyrophosphate anion. 30

Suitable brighteners and leveling agents include N-heterocyclic compounds, triphenylmethane type dyes, thiourea and thiourea derivatives. Among the thiourea derivatives which are suitable for use are tetramethylthiuram disulfate and allyl thiourea. Suitable commercial examples are Electro-Brite PC-667^{RTM} and Copper Gleam PC^{RTM}. Other suitable additives include saccharin, and o-benzaldehyde sulfonic derivatives which are especially useful in Watts nickel plating bath solutions. 35

In the preferred embodiment of the invention, metallic sites are formed by treating the respective surface with a solution comprising the metal (A) as a compound or complex, e.g., as metal-halide as exemplified by palladium-tin chloride, a double metal halide.

40 In forming metallic sites of metal (A) it has been found advantageous, following the treatment with the said solution, to expose the surface to a reducing agent. 40

In the case of the site-forming compound comprising tin, it has further been found advantageous to remove the tin-compound from the surface provided with sites. This is accomplished by a tin removing solvent such as a dilute aqueous fluoroboric acid solution or strongly basic solutions which allow formation of soluble alkali stannites. 45

In order to achieve improved shelf-life of the surfaces provided with sites it has been found advantageous to expose the surface treated with the site-providing solution to a heat treatment, e.g., at a temperature of 65 to 120°C for 10 minutes or longer. It has been found that surfaces thus treated immediately after removal from the site-providing solution may be stored for extended periods of, e.g., 9 months without detrimental influence. It is advantageous after extended storage to expose the surface provided with sites to an acidic solution, e.g., one molar sulfuric acid, for 15 to 20 minutes. 50

Suitable reducing agents mentioned above may be selected from sodium borohydride, formaldehyde, dimethylamine borane or hydroxylamine.

It has also been found advantageous to pretreat the non-metallic surface prior to the site-providing step by exposing it to a cleaner conditioner, for example, an aqueous solution containing a blend of nonionic and cationic wetting agents. Such cleaner conditioners are widely used in printed circuit and plating on plastics arts. 55

Fig. 1 is a graphical presentation showing the current potential relationship defining the difference $\Delta(E)_i = E'_i - E''_i$.

60 Fig. 2 is a graphical presentation showing the current potential relationship defining the difference $\Delta(E)_{dep} = E'_{dep} - E''_{dep}$. 60

Fig. 3 is a series of photographs showing a chronological sequence of electrodeposition produced in accordance to the method of this invention.

Figs. 1 and 2 are explained in detail on pp. 9—11 of this specification.

Fig. 3 is a sequence (a) to (f) of photographs taken at different times after the start of electrodeposition performed in accordance with this invention.

- Fig. 3a is a photograph taken after 1 minute of electrodeposition in an electroplating bath solution used in the method of the present invention. The substrate is a copper clad laminate provided with palladium metallic sites on the walls of the through holes. Copper is the metal being deposited.
- Fig. 3b is a photograph of the same substrate taken after 2 minutes of electrodeposition.
- Fig. 3c is a photograph of the same substrate taken after 3 minutes of electrodeposition.
- Fig. 3d is a photograph of the same substrate taken after 4 minutes of electrodeposition.
- Fig. 3e is a photograph of the same substrate taken after 5 minutes of electrodeposition.
- Fig. 3f is a photograph of the same substrate taken after 20 minutes of electrodeposition.
- As exemplified by this series of photographs, the metal deposit formed on the surface of the hole wall is uniform and continuous.

Example I

- This example describes metallizing the walls of holes drilled in panels cut from sheets of two-sided copper clad insulating base material of the type used in the manufacture of printed circuit boards, having a thickness of 1,6 mm and known as FR-4 epoxy glass material.

- The panels provided with holes were treated with a solution containing a cationic surfactant, a nonionic surfactant and an alkanolamine and adjusted to a pH below 4, thus cleaning and conditioning the hole wall surfaces for subsequent treatment steps.

- Subsequently, the panels were dipped into a 1% aqueous sulfuric acid solution for 5 minutes, water rinsed, treated with a sodium persulfate solution (120 g/l at a pH less than 2) for 45 seconds at 40°C to deoxidize the copper surface, and again water rinsed.

- The panels were then treated for 5 minutes in a solution containing 5 g/l stannous chloride, 225 g/l sodium chloride, and sufficient hydrochloric acid to obtain a pH of less than 0,5. After this step the panels were exposed for 5 minutes to a palladium-tin-chloride solution at 55°C with continuous agitation. The palladium-tin-chloride solution was formulated as described in Example 3 of Patent 1 306 201 and diluted to a palladium concentration of 210 mg/l by mixing it with an aqueous solution comprising 3,5 mole sodium chloride and 0,08 mole stannous chloride. After immersion in the said palladium-tin-chloride solution the panels were water rinsed, heat treated in an oven for 60 minutes at 100°C and then brushed.

- Before electroplating, the copper surfaces were deoxidized by dipping for 5 seconds in a solution of sodium persulfate. A number of the thus prepared panels were electroplated in a plating solution consisting of 0,3 mole copper sulfate, 1,8 mole sulfuric acid, and 1,3 millimole hydrogen chloride.

- The current density was 3,5 A/dm².
- After electroplating for 5 minutes, only 10% of the hole wall was covered. After electroplating for one hour, the panels were removed and the holes examined. Copper was formed partially down the walls of the hole with a large area around the mid-point or center area of the hole wall left void of copper.

- A second number of the said prepared panels were electroplated after 5 g/l of a nonionic surfactant, octylphenoxypolyethoxyethanol, was added to the copper electroplating solution. After less than 5 minutes plating, the hole walls were found to be completely covered with a continuous, void-free film of copper metal.

Example II

- Additional panels prepared by the method of Example I were electroplated in a copper plating solution which was the same as in Example I except that it contained 5 g/l of methyl violet instead of the non-ionic surfactant used in Example I and the plating potential adjusted in accordance with the present invention. After 5 minutes of electroplating, the hole walls were covered with a complete, continuous film of copper metal.

Example III

- The procedure of Example II was repeated except that methylene blue was substituted for methyl violet. Again, after 5 minutes of electroplating, the hole walls were covered with a complete, continuous film of copper.

Example IV

- The procedure of Example I was repeated except that a Watts nickel electroplating bath solution was substituted for the copper electroplating bath. The Watts nickel bath consisted of 300 g/l nickel sulfate, 30 g/l nickel chloride, and 30 g/l boric acid. Even after extended periods of plating, only incomplete plating on the hole walls was observed. Saccharin was added to the Watts nickel bath, and another panel exposed to the plating operation. A complete, continuous film of electroplated nickel quickly covered the hole walls.

Example V

The procedure of Example IV was repeated except that the Watts nickel bath contained 20 ml/l of Lecto-Nic 10-03^{RTM}, a compound comprising an o-benzaldehyde sulfonic acid. A complete, continuous film of electrodeposited nickel was obtained on the hole walls.

5 Example VI

The procedure of Example IV was repeated except that Copper Gleam PC^{RTM}, a compound used as a brightener for copper sulfate/sulfuric acid electroplating baths comprising a triphenylmethane dye, was added to the Watts nickel bath. A complete, continuous film of electroplated nickel was obtained on the hole walls.

10 Example VII

This example describes the manufacture of a printed circuit board utilizing the metallizing techniques of this invention.

Copper clad insulating sheets of FR-4 or CEM-3 grades of printed circuits basematerials were cut into convenient size panels, the holes required for plated through hole connections drilled, and the copper surfaces of the panels deburred. The panels were then treated in sequence as in Example I in a cleaning and conditioning solution, a sulfuric acid solution, a rinse, a sodium persulfate solution, another rinse, a solution comprising SnCl₂ and NaCl, and a palladium-tin-chloride solution. Subsequently, the panels were rinsed, heat treated in an oven for 20 minutes at 120°C, and brushed. The thus treated panels may be stored at this state or processed immediately without process interruption.

For further processing, the panels were provided with a plating resist mask produced by well-known photoprinting, screen-printing or other suitable processes and then subjected to a reverse current electrocleaning procedure at 3 A/dm² in a commercial alkaline cleaner solution for 45 seconds, rinsed and treated with sodium persulfate (as described above) for 5 seconds and rinsed again.

The panels were then electroplated for 5 minutes at a potential providing a current density of, appr., 3 A/dm², using a bath comprised of the following.

	Copper sulfate	75 g/l	
	Sulfuric acid	190 g/l	
	Chloride ion	70 ppm	
30	Electro-Brite ^{RTM} (PC-667)	5 ml/l	30

The resulting panels were rinsed and further copper electroplated for 40 minutes at 3 A/dm² in a bath comprised of

	Copper sulfate	75 g/l	
	Sulfuric acid	190 g/l	
35	Chloride ion	50 ppm	35
	Copper Gleam PC ^{RTM}	5 ml/l	

Alternatively, the panels, instead of undergoing the dual electroplating steps described above, were plated in a single step operation for approximately 45 minutes at 3 A/dm² in the first electroplating bath solution described above.

The panels were then rinsed and converted to printed circuit boards by the well known steps of solder plating at 2 A/dm² for 18 minutes, rinsing, resist stripping, etching with ammonical copper chloride solution, solder fusing, applying of solder mask and trimming the circuit board to size.

Example VIII

A copper clad panel was processed in accordance with Example VII up to and including the step of exposing the panel to a palladium-tin-chloride solution. This step was followed by a rinse and the subsequent immersion in a 5% fluoroboric acid solution which is a solvent for the tin component of the palladium-tin-chloride sites deposited on the walls of the holes. Then, the panel was plated at 3 A/dm² in a copper electroplating bath solution formulated in accordance with the present invention and composed as follows:

50	Copper sulfate	75 g/l	50
	Sulfuric acid	190 g/l	
	Chloride ion	50 ppm	
	Copper Gleam PC ^{RTM}	5 ml/l	

After depositing a layer of copper of a thickness of 35 μm, the panel was rinsed, dried and a positive photoresist etching mask was applied by well-known techniques, covering the desired circuit pattern including the plated through holes. The copper not protected by said mask was removed by

etching and the resist subsequently removed by standard processes, thus forming a finished printed circuit board.

Example IX

This Example describes the preparation of a printed circuit board of the multilayer type. A well known procedure was used to form a multilayer composite by combining individual layers of circuit patterns on insulating carriers and forming them into a laminate. After the through holes were produced and the smear removed from the copper layers forming parts of the hole walls, the laminate was processed as described in Example VII or VIII.

Example X

This example describes the preparation of a printed circuit board using a bare laminate not provided with a copper foil on its surface(s).

The surfaces of the panel were provided with an adhesive layer and holes with walls to be metallized, and said layer was treated by the method of Patent No. 1 187 061 making it microporous and hydrophilic. The panel was attached to an electroplating fixture to provide a conductive border forming a suitable connector area and exposed to the process steps as described in Example VIII, thus forming the desired printed circuit pattern.

Example XI

Copper clad, FR-4 epoxy glass laminate panels were provided with holes, cleaned and treated as described in Example I up to and including treatment with a palladium-tin-chloride solution. Following these steps, the panels were rinsed, dried and immersed one in each of the following reducing agents (dissolved in aqueous 1,5 mole sodium hydroxide solutions): sodium borohydride; hydroxylamine. Both panels were electroplated in accordance with the present invention for 2 minutes in the copper electroplating bath solution of Example VIII and complete, continuous films of copper were obtained on the hole walls.

Example XII

The procedure of Example XI was repeated except that an aqueous solution comprising the admixture of potassium hexachloroplatinate (IV) and stannous chloride, was substituted for the palladium-tin-chloride solution. The reducing agent used was a 1 g/l solution of sodium borohydride. The hole walls were covered with a continuous film of copper in less than 5 minutes of electroplating in accordance with the present invention.

Example XIII

The procedure of Example VIII was repeated except that a copper pyrophosphate electroplating bath was substituted for the copper sulfate/sulfuric acid bath. The copper pyrophosphate bath was of the following composition:

35	Copper	32 g/l	35
	Pyrophosphate anion	245 g/l	
	Ammonia	225 g/l	
	Temperature	52 °C	

In this solution, the pyrophosphate anion performed the function of component (C). After 5 minutes of electroplating at 4,5 A/dm² there was complete coverage of the hole walls with copper. When the procedure was repeated with another panel in the same plating bath after the addition of 1 ml/l of the conventionally used brightener for copper pyrophosphate plating bath solutions, a dimercaptiothiadiazole compound (PY61H^{RTM}), the hole walls were not plated. The dimercaptiothiadiazole is strongly adsorbed on the surface of the palladium metallic sites and prevents deposition on said sites.

Example XIV

The procedure of Example VII was repeated except that following the palladium-tin-chloride solution and rinse step, the copper clad panels were, without drying, immersed in a solution containing fluoboric acid (100 ml/l) and hydroxyethylene diamine triacetic acid (4 g/l) for 30 seconds, rinsed and then electroplated according to this invention in a copper electroplating bath solution which was the same as in Example I except that as the non-ionic surfactant Pluronic F-127^{RTM}, a block copolymer of propylene- and ethylene-oxides, was present in the solution as component (C) in a concentration of 0,2 g/l. After 5 minutes of electroplating at a potential providing a current density of 3,8 A/dm², the hole walls were found to be covered with a complete, continuous film of copper.

Example XV

In the following Examples A to O the procedure of Example XIV was repeated, with Example A+B

using the same and Examples C to O using different surfactants as component (C), and with concentrations, current densities and plating times as shown hereinafter. The result, after electroplating, was in all cases a complete, void-free, continuous film of copper covering the hole walls.

5	Example	Compound	Conc. g/l	Current density A/dm ²	Plating time min.	5
	A	Pluronic F-127 ^{RTM}	0,2	3,8	5	
	B	Pluronic F-127 ^{RTM}	0,2	5,92	3	
	C	Carbowax 1540 ^{RTM}	0,3	3,8	5	
10	D	Carbowax 1540 ^{RTM}	0,3	5,92	3	10
	E	Pluronic F-68 ^{RTM}	1,0	3,8	5	
	F	Pluronic F-68 ^{RTM}	1,0	5,92	3	
	G	Pluronic L-42 ^{RTM}	1,0	3,8	5	
	H	Polyox WSR 80 ^{RTM}	1,0	3,8	15	
15	I	Carbowax 4000 ^{RTM}	0,5	3,8	15	15
	J	Olin 10G ^{RTM}	0,5	3,8	15	
	K	Olin 6G ^{RTM}	0,5	3,8	15	
	L	Carbowax 20M ^{RTM}	0,5	3,8	15	
	M	Pluronic L-64 ^{RTM}	0,5	3,8	15	
20	N	Tergitol Min Foam 1X ^{RTM}	0,5	3,8	15	20
	O	Carbowax 600 ^{RTM}	1,0	3,8	15	

Pluronic^{RTM} stands for a series of block copolymers of polyoxyethylene and polyoxypropylene. Pluronic F-127^{RTM} has a polyoxypropylene base of about 70 oxypropylene units to which are attached two polyethylene chains which contain in aggregate about 300 oxyethylene groups. In Pluronic F-68^{RTM} the polyoxypropylene portion contains approximately 160 units. Pluronic L-42^{RTM} has approximately twenty oxypropylene units and fifteen oxyethylene units.

Polyox WSR 80^{RTM} is a polyoxyethylene compound with an average molecular weight of 200.000.

Olin 6G^{RTM} and Olin 10G^{RTM} are alkyl phenyl polyoxyethylene compounds with six and ten oxyethylene group, respectively.

Tergitol Min. Foam 1X^{RTM} is a polyoxypropylene-polyoxyethylene compound of a linear alcohol.

Example XVI

The procedure of Example XIV was repeated except that the electroplating bath solution was a nickel bath solution comprised of the following:

35	NiSO ₄ 6H ₂ O	195 g/l	35
	NiCl ₂ 6H ₂ O	175 g/l	
	H ₃ BO ₃	40 g/l	
	pH	1,5	
	Temperature	46 °C	

40 The nonionic surfactant added to this solution as component (C) was Carbowax 1540 in a concentration of 0,1 g/l.

After electroplating at a potential providing 3,8 A/dm² for 15 minutes, the hole walls were covered with a complete, continuous film of nickel.

Example XVII

45 In order to more fully demonstrate the usefulness of polyoxyethylene groups in carrying out the method according to this invention, sodium lauryl sulfate, an anionic surfactant widely used in the electroplating industry, and recommended for use in acid copper sulfate electroplating bath solutions, was tested as follows. The procedure of Example XIV was repeated except that in one copper electroplating bath 1,0 g/l sodium lauryl sulfate (Duponol C^{RTM}) was added as the surfactant instead of Pluronic F-127^{RTM}, and in a second and a third electroplating bath solution 1,0 g/l ammonium polyether sulfate and 1,0 g/l ammonium lauryl polyether sulfate (Sipon E^{RTM} and Sipon A^{RTM}) were used instead of Pluronic F-127^{RTM}. After 5 minutes plating time, both the polyether sulfate and polyether lauryl sulfate containing electroplating bath solutions produced complete, continuous films of copper covering the hole walls, while even 15 minutes electroplating in the lauryl sulfate containing bath solution did not cover the hole walls.

This experiment shows that a simple linear anionic surfactant, lauryl sulfate, was ineffective for purposes of this invention. When the surfactant is selected in accordance to the teachings of this

invention, such as when the lauryl sulfate structure was modified by the polyether group, it became effective as component (C).

Example XVIII

The procedure of Example VIII was repeated except that substituted thioureas were substituted for Copper Gleam PC^{RTM}. In one copper electroplating bath solution, 5 mg/l of tetramethylthiuram disulfide and in a second such solution 0,8 g/l of allyl thiourea were used, respectively, as component (C). After electroplating for 15 minutes at a potential providing 3,8 A/dm² the hole walls of printed circuit boards plated in either solution were covered with a continuous film of copper.

It should be understood by those skilled in the art that various modifications may be made in the present invention without departing from the spirit and scope thereof as described in the specification and defined in the appended claims.

Claims

1. A method for metallizing a non metallic surface by electroplating in a vessel provided with a counter-electrode and containing an electroplating bath solution comprising in ionic form a metal (B) to be electroplated, said surface being provided with a connector area, said connector area being located outside of the non-metallic surface area to be electroplated, characterized by the steps comprising (a) forming a plurality of metallic sites on said surface, said sites comprising or consisting of a metal (A), said metal (A) being different from said metal (B) to be deposited on said surface by electroplating; and (b) exposing said surface including at least a portion of said connector area to the electroplating bath solution, said solution having a defined conductivity and further comprising one or more component(s) (C) which cause preferential deposition of metal (B) on said metallic sites comprising or consisting of metal (A), compared to the deposition on surfaces consisting of, or formed by, the species of the electrodeposited metal (B); and (c) applying a potential to the connector area at the counter electrode which is sufficient to initiate and cause preferential deposition of metal (B) on said sites comprising or consisting of metal (A), for a time sufficient for forming a substantially uniform deposit of desired thickness.
2. The method of claim 1 characterized in that said component (C) preferentially attaches itself to a surface of the species of metal (B) compared to the surface of the species of metal (A), thus substantially inhibiting or reducing the plating reaction on surfaces formed by metal (B) without substantially interfering with the plating reaction on surfaces formed by the species of the site metal (A).
3. The method of claim 2, characterized in that said component (C) is increasing the overpotential on surfaces formed by metal (B).
4. The method of claim 1, characterized in that said component (C) preferentially attaches itself to the species of site metal (A), said component (C) substantially increasing the plating reaction on surfaces formed by site metal (A) compared to the plating reaction on surfaces of the species of metal (B).
5. The method of claim 4, characterized in that said component (C) reduces the overpotential thus increasing the plating reaction compared to the plating reaction on surfaces of the species of metal (B).
6. The method of claims 1 to 5, characterized in that said component (C) is selected from dyes, surfactants, chelating agents, brighteners and leveling agents.
7. The method of claim 6, characterized in that said component (C) is a dye selected from methylene blue and methyl violet.
8. The method of claim 6, characterized in that said component (C) is a surfactant selected from alkylphenoxypolyethoxyethanols, nonionic fluorocarbon surfactants, polyoxyethylene compounds, block copolymers of polyoxyethylene and polyoxypropylene.
9. The method of claim 8, characterized in that said component (C) is selected from compounds containing 4 to 100 000 oxyethylene groups.
10. The method of claim 9, characterized in that said compound (C) contains 20 to 50 oxyethylene groups.
11. The method of claim 8, characterized in that said compound (C) is selected from ethylene oxide-propylene oxide copolymers containing 10 to 400 oxyethylene groups.
12. The method of claim 6, characterized in that said component (C) is a chelating agent selected from 2,4,6-(2-pyridyl)-s-triazine and the pyrophosphate anion.
13. The method of claim 6, characterized in that said component (C) comprises a brightener and/or leveling agent selected from N-heterocyclic compounds and triphenyl methane dyes, thiourea, thiourea derivatives such as allyl thioureas and tetramethylthiuram disulfide, saccharin and o-benzaldehyde sulfonic acid derivatives.
14. The method of claim 6, characterized in that said component (C) is Electro-Brite PC-667^{RTM}.
15. The method of claim 6, characterized in that said component (C) is Copper Gleam PC^{RTM}.
16. The method of claim 1, characterized in that the conductivity of the electroplating bath solution and the potential applied to the connector area and the counter-electrode are selected sufficiently high to achieve a rate of deposition on the surface of the species of the site metal (A) which

is at least one order, and preferably, two orders of magnitude higher than the deposition rate on the surface of the species of metal (B).

17. The method of claim 16, characterized in that the conductivity is adjusted to the highest value permissible with respect to the other plating parameters.

5 18. The method of claim 16, characterized in that the potential is adjusted to compensate for the potential drop on the resistive path formed by the plating bath solution between the connector area and the metallic sites consisting of, or comprising metal (A), and between such neighboring sites. 5

19. The method of claim 18, characterized in that the potential is adjusted to the highest value permissible with respect to the other plating parameters.

10 20. The method of claims 1 to 19, characterized in that metal (A) and metal (B) are selected from Groups Ib and VIII of the Periodic Table of Elements, and that metal (A) differs from metal (B). 10

21. The method of claims 1 to 20 characterized in that metals (A) and (B) are selected so that the potential for the deposition of metal (B) on metal (A) is less negative than the potential for the deposition of metal (B) on itself under the conditions provided by the plating operation.

15 22. The method of claims 20 or 21, characterized in that metal (A) is selected from palladium, platinum, silver or gold. 15

23. The method of claims 20 or 21, characterized in that metal (B) is selected from copper or nickel.

24. The method of claims 1 to 23, characterized in that the site formation step comprises 20 employing metal (A) in solution as a compound or complex. 20

25. The method of claim 24, characterized in that the compound is a metal halide or double metal halide.

26. The method of claim 25, characterized in that the double metal halide is a palladium-tin-chloride.

25 27. The method of claims 24 to 26, characterized in that the solution comprises metal (A) and a tin-halide; and that the treated surface is subsequently exposed to a solvent for tin-compounds. 25

28. The method of claims 1 to 27, characterized in that the plurality of metal sites of metal (A) is formed by treating the non-metallic surface with a solution comprising metal (A) and subsequently exposing said surface to heat or to a reducing agent.

30 29. The method of claim 28, characterized in that said heat-treatment is effected at a temperature in the range of 65 to 120°C and for at least 10 minutes. 30

30. The method of claim 28, characterized in that said reducing agent is selected from sodium borohydride, formaldehyde, dimethylamine borane and hydroxylamine.

35 31. The method of claim 1, characterized in that it further comprises the steps of terminating the deposition of metal (B) after establishing a continuous film of metal (B) of desired thickness over the non-metallic surface; and by electrolytically depositing one or more metal layers on said film or part of said film. 35

40 32. The method of claim 31, characterized in that at least two electroplating bath solutions of different composition are employed; and that the first used solution comprises components which maximize the rate of deposition on metal (A); and that the electroplating bath solutions employed subsequently are formulated for optimizing the properties of the respective metal deposit formed. 40

45 33. The method of claims 1 to 32, characterized in that it further comprises the steps of forming holes in a copper clad insulating sheet, or in a laminate formed by a plurality of such sheets; and providing a negative image resist layer on the surface of said copper clad sheet or laminate, which layer leaves exposed the areas corresponding to a desired conductor pattern including the walls of said holes provided with said sites of metal (A); and, after the electroplating step, removing said resist layer and etching away the metal in the areas which have been covered by said resist layer thus forming a printed circuit board. 45

50 34. The method of claims 1 to 32, characterized in that it further comprises the steps of forming holes in a copper clad insulating sheet, or in a laminate formed by a plurality of such sheets; and, subsequent to the electroplating step, providing a positive image resist layer on the surface of said copper clad sheet or laminate, said resist layer covering the areas corresponding to the desired circuit pattern including the holes; and etching away the metal not covered by the positive image resist layer thus forming a printed circuit board. 50

55 35. The method of claims 1 to 32, characterized in that it further comprises the step of providing an insulating sheet with a connector area placed outside of the area to be electroplated with metal (B). 55

36. The method of claim 35, characterized in that the connector area is shaped window-frame like and is arranged in small areas along the edges of said sheet.

37. The method of claims 35 or 36, characterized in that the insulating sheet is provided with holes prior to forming said metallic sites of metal (A).

38. The method of claims 35 to 37, characterized in that after forming said sites of metal (A) the surface is provided with a negative image resist layer leaving exposed the areas corresponding to the
5 desired conductor pattern including the walls of said holes and subsequently electrodepositing metal (B) thus forming the circuit pattern of a printed circuit board. 5

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